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# ELECTRON CAPTURE KINETICS

Boston College

David L. McFadden

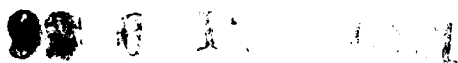


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13. ABSTRACT (Maximum 200 words)  In this report we discuss experiments designed to measure electron cyclotron resonance detention of electrons, for candidate molecules not requiring synthetic preparation. We also developed techniques for preparation of new candidate species, and measured rate constants for electron attachment to these species, and identified negative species produced by electron attachment.					
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## OTHER PARTICIPANTS AND TITLES:

Robert G. Levy, graduate student research assistant.

Cheng-ping Tsai, graduate student research assistant.

## A. TECHNICAL PROGRESS ACHIEVED ON EFFORT:

A new discharge flow apparatus was designed, constructed and installed in the Electron Cyclotron Resonance (ECR) apparatus. Several modifications of the previous design included: 1) Enlargement of the access collats on the ECR cavity to accommodate a 3.5 cm diameter flow tube; 2) Provision for movement of the electromagnet and cavity over a distance of 70 cm to facilitate direct measurement of the ambipolar diffusion coefficient; 3) Addition of 5 reactant inlets, each with a mixing chamber and multiple inlet openings over the entire circumference of the flow tube; 4) Addition of permanent electrodes for the purpose of plasma velocity measurements; 5) Addition of gas handling manifold for switching reactant gases among the five reactant inlets.

Experiments related to electron capture kinetics included first the determination of conditions where ambipolar diffusion obtained. Previous workers in the field have operated with considerably larger diameter flow tubes (8 cm) and much lower pressures (0.5 Torr). The maximum diameter that the ECR cavity can accommodate is 3.5 cm, thus higher pressures must be used to slow down the diffusion to the wall. Diffusion was thoroughly investigated, and the conditions for ambipolar diffusion determined. It is necessary to measure the diffusion coefficient in each kinetics experiment for the data analysis. Rate constants for  $\text{SF}_6$  were measured as a check of the new apparatus and the procedures. At present the values being obtained are close but a bit low compared to values taken from the literature

Absolute rate constants for electron attachment reactions of  $\text{CF}_3\text{Mn}(\text{CO})_5$ ,  $\text{CF}_3\text{Co}(\text{CO})_4$  and  $\text{C}_2\text{F}_5\text{Co}(\text{CO})_4$  have been measured in a gas flow system with electron cyclotron resonance (ECR) detection. Free electrons were generated by Penning ionization of Argon gas by Helium metastables produced in a low power radio-frequency discharge. The pressure was 2.3-2.5 Torr. The rate constants at 293 K in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  are  $(3.5 \pm 0.6) \times 10^{-7}$  for  $\text{CF}_3\text{Mn}(\text{CO})_5$ ;  $(2.0 \pm 0.4) \times 10^{-7}$  for  $\text{CF}_3\text{Co}(\text{CO})_4$ ; and  $(1.8 \pm 0.3) \times 10^{-7}$  for  $\text{C}_2\text{F}_5\text{Co}(\text{CO})_4$ . Negative ion mass spectra indicate that nondissociative attachment is important at thermal electron energy. The cross section for non-dissociative capture falls rapidly with increasing electron energy. Dissociative product channels are also observed. Electron capture rate constants for several additional molecules are presented and compared with values from the literature. The rate constants in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  are  $2.8 \times 10^{-7}$  for  $\text{SF}_6$ ;  $3.7 \times 10^{-7}$  for  $\text{CCl}_4$ ;  $3.1 \times 10^{-7}$  for  $\text{CFCl}_3$ ;  $1.8 \times 10^{-9}$  for  $\text{CF}_2\text{Cl}_2$ ;  $1.5 \times 10^{-8}$  for  $\text{CF}_3\text{Br}$ ;  $3.8 \times 10^{-9}$  for  $\text{CHCl}_3$ ; and  $1.2 \times 10^{-8}$  for  $\text{C}_2\text{F}_3\text{Cl}_3$ .

Low pressure flames in conjunction with the electron cyclotron resonance method of detection for electrons was investigated to study the kinetics of electron attachment at very high temperatures ( $>2000 \text{ C}$ ) in a combustion system. A low pressure flame apparatus that can be installed inside the room temperature cavity of the ECR apparatus was designed, constructed, and tested. A low pressure flame of acetylene and oxygen at a pressure between 20 and 40 Torr was successfully established. This flame produces a relatively large concentration of electrons by a chemiionization mechanism. Initial studies of electron attachment of  $\text{SF}_6$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CF}_3\text{Br}$  were conducted.  $\text{SF}_6$  was found to be the most effective in the flame, though the results must be considered preliminary.

B. TRAVEL: None

#### C. PRESENTATIONS AND PUBLICATIONS:

Electron Attachment Reactions of Perfluoroalkyl Transition Metal Carbonyls: Rate Constants and Product Analysis, Christopher J. Marotta, Cheng-ping Tsai and David L. McFadden, J. Chem. Phys. (in press, August 15, 1989 issue).

#### D. LEVEL OF EFFORT BY EACH CONTRIBUTOR (IN MAN-MONTHS OR MAN-HOURS):

David L. McFadden, P. I., 100%, 1 month, \$4333.

Robert G. Levy, grad. research asst., 100%, 6 months, \$5280.

Cheng-ping Tsai, grad. research asst., 100%, 6 months, \$4500.

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